

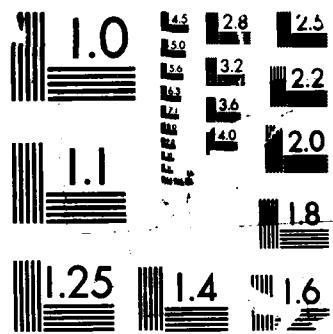
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THEORETICAL INVESTIGATIONS OF NITROCUBANE DECOMPOSITION 1/1
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Theoretical Investigations of Nitrocubane Decomposition

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1987

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The development of propulsion systems for the strategic defense initiative requires propellants which are highly energetic yet stable. An understanding of the factors controlling the stabilities of propellents requires knowledge of the detailed microscopic decomposition pathways and their relative rates. Experimental investigations can be limited by the inability to study individual elementary reaction steps, and the inability to attain the temperatures and pressures experienced in a detonation. Theoretical studies are a complementary tool to experiments and provide insight into the dynamics of the elementary reactions as well as crucial kinetic data. The theoretical calculation of the chemical reaction rate is a two step process: first, the interaction energies between the atoms is obtained from an electronic structure calculation, followed by a dynamical calculation of the rate. Currently, these methods can be routinely applied to provide accurate kinetic data only for relatively small systems. The goal of the present research is to extend and validate these methods for the treatment of much larger molecules such as those found in the decomposition of nitro derivatives of cubanes.

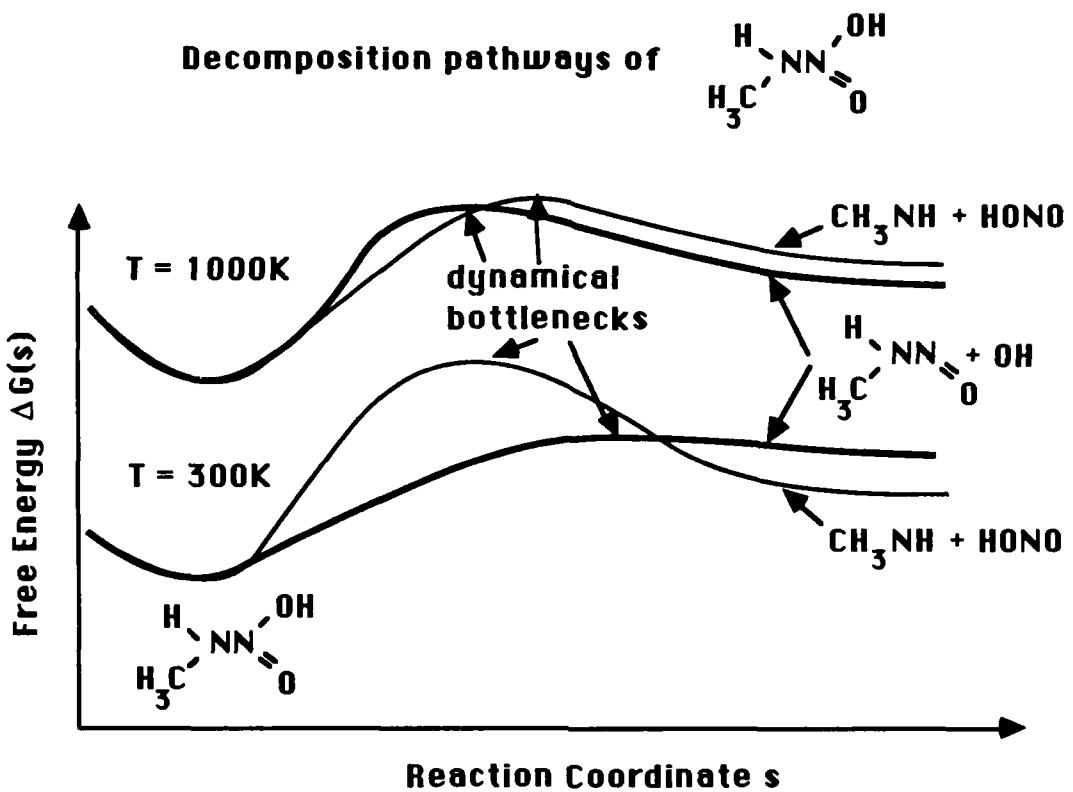
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This research entails a collaboration with Dr. Carl Melius of Sandia National Laboratory, Livermore, California which brings together unique capabilities in electronic structure and dynamics calculations. Thermal rate constants are calculated by variational transition state theory (VTST) using information about the potential energy surface from electronic structure calculations using the bond additivity correction based upon Møller-Plesset fourth order perturbation theory (BAC-MP4). The potential interactions include semiempirical corrections to high quality electronic structure calculations and represent the best possible estimates of the energetics. The use of variational transition state theory in these calculations is mandated for several reasons: (1) it includes the factors most important in controlling the rate of chemical reactions and provides reliable predictions of rates for a variety of gas-phase reactions; (2) it is capable of utilizing limited information about the potential along the minimum energy path without requiring a global potential energy surface; (3) because of the nature of the semiempirical potential information utilized in this work, the variational procedure to locate the dynamical bottleneck is necessary; and (4) it provides a consistent method for incorporating quantum mechanical tunneling effects which are crucial for accurate predictions of the rates, especially at temperatures below 600 K. The sensitivity of the computed rate constants to the level of theory is studied for a relatively small system (involving five atoms) for which high levels of theory can be afforded. Comparison is also made between the computed and experimental rates as further validation of the methods. These studies indicate that accurate rate constants (to within about 50%) can be obtained for a modest computational effort – several hours of Cray 1s computer time were required to obtain rates for temperatures from 200 to 2400 K – thus establishing the feasibility of this theoretical approach.

In order to treat reactions involving very large molecules (such as the initial unimolecular decomposition step in nitrocubane combustion) approximate methods for estimating kinetic parameters are needed. As a first step in this direction, a systematic study of hydrogen attack on a series of nitro containing molecules are performed to examine the effects of substituents on the computed reaction rates. In addition, a new thermochemical kinetic analysis is presented which includes important dynamical effects that are crucial for reliable predictions of thermal rates. This new analysis is the basis for methods of estimating kinetic parameters for large polyatomic systems from bond and group additivity relationships, but using information about potential energy surfaces for smaller analogous reactions.

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Variational transition state theory rate

$$k^{\text{VTT}} = \frac{k_B T}{h} \exp(\Delta G_{\text{max}} / RT)$$

ΔG_{max} = free energy at the dynamical bottleneck
 R = Gas constant

Reliable estimates of the rates are obtained using semiempirical corrections to *ab initio* electronic structure information (BAC-MP4) to compute the free energy.

The free energy can be analyzed by thermochemical kinetic models to provide estimates of rates for reaction containing similar groups (group additivity relationships).

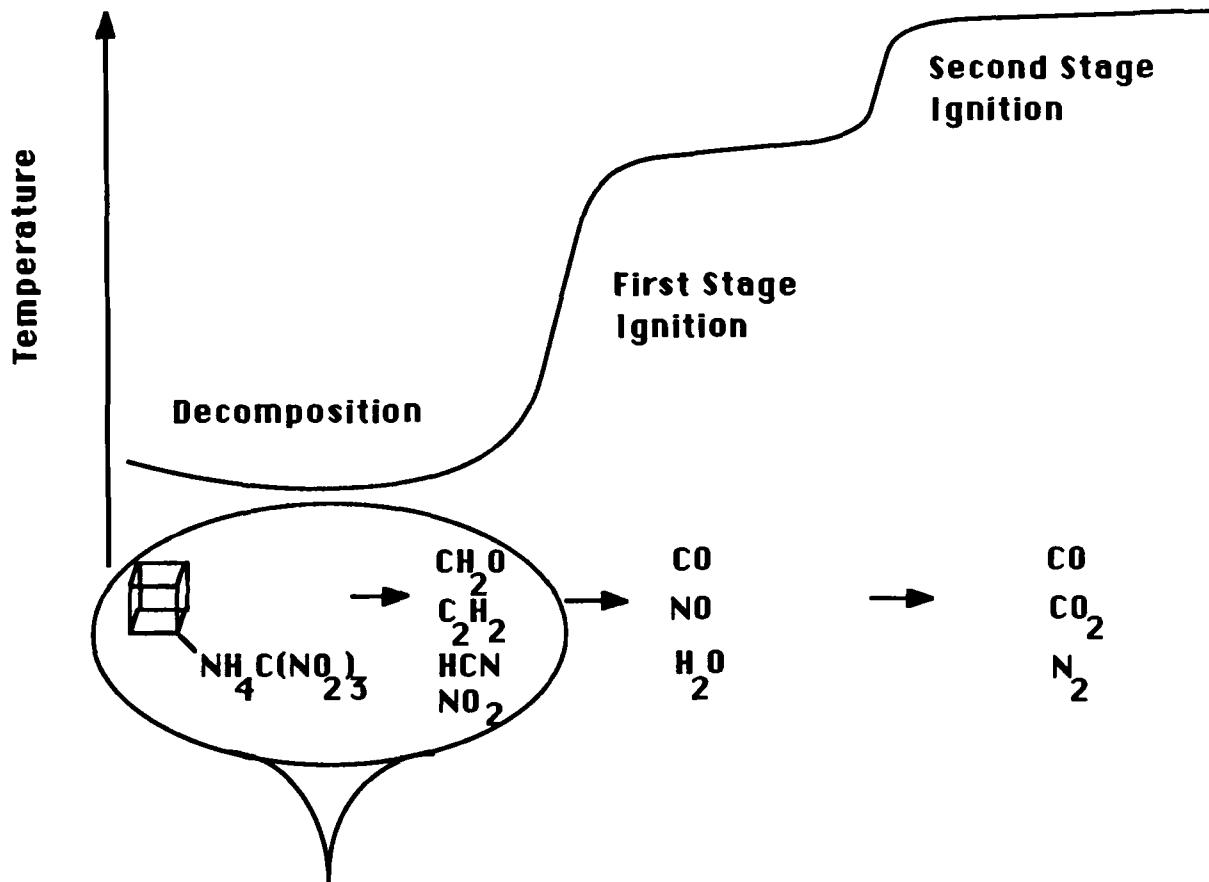
The present calculations provide a new database for thermochemical kinetic models. This database includes the effect of variationally locating the dynamical bottleneck and also includes important quantum mechanical tunneling effects.

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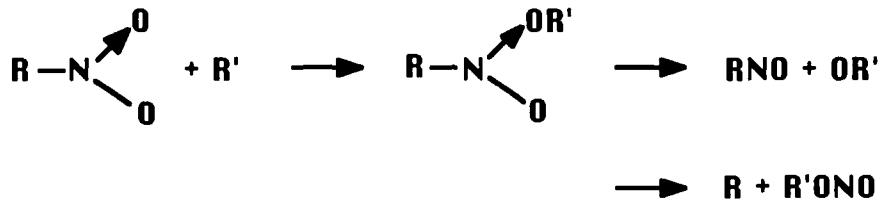
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Ignition of Energetic Cubanes



Radical attack on nitro groups is important in the early stages of decomposition, e.g.



Thermochemical and chemical kinetic rate data required as input are obtained from theoretical calculations (BAC-MP4 for interaction potentials and UTST for dynamical calculations of the rates).

Models of ignition provide detailed insight into complex processes, e.g. species concentration.

Sensitivity analysis identifies crucial reaction pathways and critical rate parameters.

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